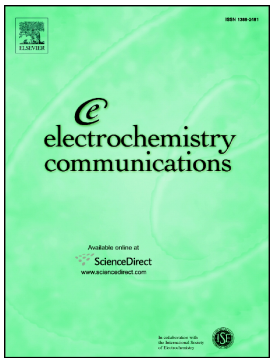

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Requirement of Initial Long-Range Substrate Structure in Unusual CO Pre-oxidation on Pt(111) Electrodes

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Abstract

The activation pathway of CO electro-oxidation at low potentials is frequently favored on a catalyst with surface defects. Here, we report a discovery in which an *initial* long-range substrate structure is required for the activation of an unusual CO pre-oxidation reaction pathway on Pt(111) surfaces which have been flame annealed and then cooled in a CO atmosphere. In contrast to current understanding about the oxidation of CO on Pt, the activation of this reaction pathway is inhibited as the (111) planes become defect-rich.

Keywords: Electrocatalysis, surface structure-sensitive, Pt electrode, CO pre-oxidation.

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1. Introduction

Studies of the electrochemical oxidation of CO on Pt have revealed that the overall rate of reaction is strongly dependent on the structure of the Pt surface [1-4]. Although the standard potential (E^0) for the reaction $CO_{(g)} + H_2O_{(l)} \rightleftarrows CO_{2(g)} + 2H^+ + 2e^-$ is ~-0.104 V_{SHE} (pH = 0), the onset potential of this reaction on Pt is only ~0.7 *vs* V_{RHE} at ~25 °C. However, the onset potential is influenced by the history of the CO adlayer [5], with lower values for those CO adlayers formed at potentials corresponding to hydrogen underpotential deposition (H_{UPD}) [6-8]. Moreover, in CO stripping experiments, it was shown that the activation pathways of CO electro-oxidation at low potentials, or CO pre-oxidation (on stepped Pt surfaces in acid media), only occurred on defected catalyst surfaces saturated with CO_{ads} (ensured with at least a small amount of CO in solution), whose adlayers were formed at potentials corresponding to H_{UPD} [9]. Under this condition of CO pre-oxidation on stepped Pt surfaces, the most catalytically active sites were the concave ones, corresponding to the sites at the bottom side of the (111) terraces, close to the steps [9]. Hence, from the kinetics viewpoint, the most interesting aspects concerning the electrocatalysis of CO oxidation are related to the reaction pathways activated at potentials that are low or closer to E^0.

Generally, among the Pt basal planes (Pt(111), Pt(100), and Pt(110)), the lowest catalytic activity towards CO electro-oxidation is shown by the Pt(111) plane, whose activity is improved by the introduction of steps and/or defects [1, 2, 10]. Nevertheless, in order to evaluate the catalytic activity of single crystals, it is fundamental to have a good method for preparation of the materials, with the most widely adopted procedure for the preparation of well-ordered Pt(111) electrodes being the established Clavilier protocol [11]. It has been observed that the state or structure of Pt surfaces is influenced by the chemical nature of the atmosphere, whether reductive (Ar/H_2, Ar/CO, etc.), oxidative (air, Ar/air, etc.), or neutral (Ar, Ar/N_2, etc.), used for cooling flame-annealed Pt crystals [12, 13]. For Pt(110) crystal, a Pt(110)-(2×1) or Pt(110)-(1×1) structure is obtained for crystals cooled in Ar/H_2 or CO atmospheres, respectively [14, 15]. Normally, an oxidative atmosphere rich in O_2 results in a reconstructed surface [12, 13, 16]. The present work investigates the catalytic activity of Pt(111) cooled in a CO atmosphere, as monitored by CO electro-oxidation.

2. Experimental Section

The following beady-type electrodes were employed as working electrodes: Pt(111), Pt(20,20,19), Pt(13,13,12), Pt(554), and Pt(332), which consisted of "infinite", 39, 25, 9 and 5 atom-width terraces, respectively, periodically interrupted by (110) monoatomic steps. The counter electrode was a Pt wire and the reference electrode was a reversible hydrogen electrode. A 0.1 M $HClO_4$ (Aldrich,70%) solution was prepared using ultrapure water (18.2 MΩ cm). The gases employed were CO (Alpha Gas,99.997 %) and Ar (Alpha Gas,N50). Information concerning electrode preparation and CO adlayer formation is provided in the description of the experiments. All the experiments were carried out at 25 ^{o}C.

3. Results

3.1. Unusual CO Pre-oxidation

Firstly, cyclic voltammograms were recorded for each Pt crystal in electrolyte only (Figure 1A), in order to show that the solution was free of impurities and that the crystal surfaces were very well ordered. Specifically, each crystal was flame-annealed and cooled in an Ar/H_2 atmosphere, followed by recording the voltammogram. Different upper potential limits were selected for each crystal, aiming at preservation of the state of the surface. Details of the features of the voltammograms are provided elsewhere [17].

Two procedures were adopted for recording the CO stripping. In the first procedure, the CO adlayer was deposited at 0.100 V_{RHE}. In each experiment, the Pt crystal was flame-annealed and then cooled in a stream of Ar/H_2, at room temperature (25 ^{o}C), in a vessel partially filled with ultrapure water. Next, the cooled electrode was quickly transferred to the electrochemical cell, together with a drop of water, and was polarized at 0.100 V_{RHE}. After recording a blank reading, a CO adlayer was deposited at 0.100 V_{RHE}, by bubbling CO gas through the solution for 5 min, after which Ar was bubbled through the solution for 20 min, allowing complete elimination of non-adsorbed CO. As expected, the results (Figures 1B-1F, black lines) showed the presence of a single CO oxidation peak in all the CO stripping voltammograms. Moreover, no Pt surface had catalytic activity at around 0.6 V (see inset), because non-adsorbed CO was completely eliminated from the solution. The peak potentials of CO oxidation shifted to lower values as the step density increased, from ~0.83 V for quasi-perfect Pt(111) to ~0.74 V for Pt(332). The Pt(332) surface possessed the highest step density among all the electrodes used. For the quasi-perfect Pt(111), the total CO coverage was $\theta_{CO} \simeq 0.67$ (estimated by considering the potential of

zero total charge, $E_{pztc} \simeq 0.35$ V_{RHE}), while the CO coverage on Pt(332) was $\theta_{CO} \simeq 0.62$ ($E_{pztc} \simeq 0.24$ V_{RHE}).

In the second procedure for preparation of the electrode and deposition of the CO adlayer, the flame-annealed electrode was cooled in a vessel through which a stream of CO gas (free of oxygen) was injected. In this procedure, a CO layer remained on the electrode while it was cooled to room temperature. The electrode covered with CO was quickly transferred to the electrochemical cell and voltammetric CO stripping was performed (Figures 1B-1F, orange lines). Two CO oxidation peaks can be seen in the voltammograms. A peak at ~0.65 V was due to a type of CO pre-oxidation. The magnitude of this CO pre-oxidation process was higher for the Pt(111) electrode, but diminished on the stepped surfaces as the density of steps increased, while this CO oxidation process was not present in the case of the flame-annealed Pt(332) cooled in a CO atmosphere. The peak potential of the CO pre-oxidation was apparently not sensitive to the steps density. On the other hand, the main CO oxidation peak shifted to lower values with increase of the steps density. For the Pt(111) electrode cooled in CO, $\theta_{CO} = 0.58 \pm 0.05$.

The CO pre-oxidation was not observed for flame-annealed polycrystalline Pt cooled in a CO atmosphere (experiments not shown).

3.2. Partial CO Stripping and Catalytic Activity after CO Stripping

In order to obtain more information about the CO pre-oxidation on the Pt(111) electrodes cooled in a CO atmosphere, experiments were carried out in which a CO adlayer was partially oxidized. Specifically, a CO adlayer formed during cooling of the electrode was oxidized in two steps. In the first step (Figure2A, black line), the potential was swept up to a value sufficient to achieve the CO pre-oxidation, and was then stepped to 0.100 V_{RHE}. In a subsequent step (Figure 2A, orange line), the potential window was extended up to 0.85 V, which was sufficient to completely remove the remaining CO layer, after which a blank was recorded. Also included was a blank voltammogram for a Pt(111) electrode cooled in an Ar/H_2 atmosphere (Figure 2A, blue line). The results revealed several notable features. Firstly, after the CO pre-oxidation, no catalytic activity was observed in the potential range in which it took place. Secondly, the CO pre-oxidation apparently did not influence the potential of the main CO oxidation peak, since it was virtually identical (Figure 2, red line) to that in the experiment in which the CO adlayer

was oxidized at once (Figure 1B, orange line). Thirdly, the hydrogen regions of these two blanks (blue and orange lines) were completely superimposed, while no features were observed at ~0.130 or ~0.280 V_{RHE}, related to steps/defects on the Pt surfaces, suggesting a "crystalline ordering" of the surface after CO stripping. The integrated charge from 0.06 to 0.35 V for the blanks was ~164 μC cm^{-2} for both Pt(111) surfaces.

In the following experiments, shown in Figure 2B, after formation of a CO adlayer by cooling a flamed-annealed Pt(111) electrode in CO (red line), the electrode was (without further flame annealing) covered by CO adlayer formed at 0.100 V_{RHE} (olive line). These two CO stripping experiments can be compared to the result for CO stripping from a fresh flame-annealed electrode cooled in an Ar/H_2 atmosphere (black line), for which the CO adlayer was deposited at 0.100 V_{RHE}. This evidenced that the history of the CO adlayer determined the activation of the CO oxidation reaction pathway at low potentials.

3.3. Influence of CO in Solution on Catalytic Activity of a Pt(111) Surface

As shown in Figure 1B (black line), in absence of CO solution, no catalytic activity was detected at around 0.6 V for a Pt(111) electrode whose CO adlayer was deposited at 0.100 V_{RHE}. However, the onset potential of CO oxidation is low in the presence of CO in the solution. Hence, a series of experiments were performed to determine the influence of solution CO on the catalytic activity of a quasi-perfect Pt(111) electrode preconditioned in an Ar/H_2 atmosphere. The CO was admitted into the solution with the potential at 0.100 V_{RHE}. After saturation of the solution with CO, it was then degassed by passing a flow of Ar for 6, 10, and 50 min (Figure3). In order to improve definition of the onset potential for CO oxidation, the experiments were carried out at a scan rate of 20 mV s^{-1}. As shown in Figure 3, for partially degassed solution, the onset potential of CO oxidation was ~0.54 V_{RHE}. When the solution was degassed for 50 min (Figure 3, olive line), no catalytic activity was observed at around ~0.62 or ~0.69 V. However, the oxidation profile did not resemble that obtained with pre-oxidation of CO on the Pt(111).

4. General Discussion

This paper reports that the history of a CO adlayer on a Pt(111) surface influenced the activation pathways of CO electro-oxidation at low potentials. Surprisingly, the pathway of the CO pre-oxidation was inhibited for defected Pt(111) surfaces. This was in contrast to the well-known CO pre-oxidation pathway on stepped Pt surfaces [9], in which

the presence of defects on the catalyst surface is required for activation of the CO pre-oxidation, *i.e.*, involving those sites at the bottom side of the steps or (111) terrace sites. On the other hand, the pre-oxidation observed for CO oxidation on a flame-annealed Pt(111) electrode cooled in CO atmosphere might be related to the CO_{ads} superstructure on the (111) facets rather than a true catalytic effect. Thus, there are differences in CO pre-oxidation, depending on both electrode pre-conditioning and CO adsorption conditions. For a well ordered Pt(111) surface, depending on the electrode potential and the presence of CO in the solution, the CO superstructure imaged by *in situ* STM was found to be *p*(2×2)-3CO (at -0.25 V_{SCE}; $\theta_{CO} \simeq 0.75$) or ($\sqrt{19}\times\sqrt{19}$)*R*23.4º-13CO (at 0.1 V_{SCE}; $\theta_{CO} \simeq 0.68$) [18]. Hence, it is unlikely that the CO_{ads} superstructure on a flame-annealed Pt(111) electrode cooled in a CO atmosphere ($\theta_{CO} = 0.58 \pm 0.05$) was one of these superstructures. In the present case, the existence of an *initial* long-range structure at the (111) plane was required to ensure activation of the pathways of CO electro-oxidation at low potentials. However, after CO stripping, a flame-annealed Pt(111) electrode cooled in CO presented greater activity than an electrode cooled in Ar/H_2 (Figure2B), suggesting that the structural integrity of the (111)-(1×1) could undergo changes after CO stripping, although features related to defects were not observed in the blank voltammogram obtained post CO stripping (Figure2A).

5. Main Conclusions

A new aspect of high catalytic activity pathways involved in CO electro-oxidation was revealed. It was demonstrated that the activation pathway of CO pre-oxidation also depended on the way that a CO adlayer was deposited on a Pt(111) surface. Unexpectedly, for a CO adlayer deposited during cooling of the Pt(111) surface in a CO atmosphere, the presence of crystalline steps (or random features) on the (111) plane inhibited activation of the CO pre-oxidation pathway. It could be concluded that an *initial* long-range structure of the (111) substrate governed the catalytic activity at these (111) facets.

Acknowledgments

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Figures

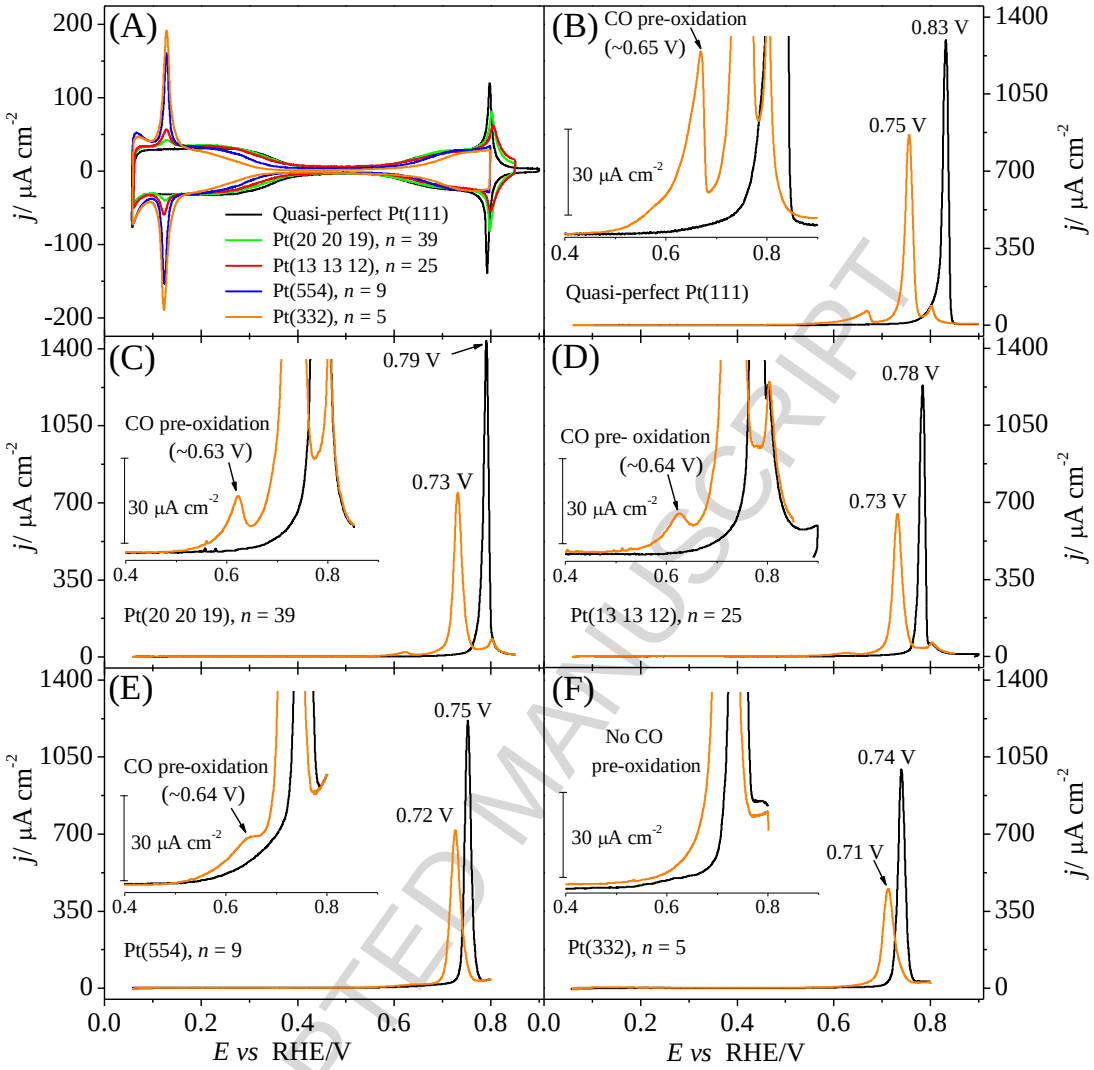


Figure 1. Pt(111) electrodes. (A) Blank voltammetries; (B-F, orange lines) CO stripping on a flame-annealed electrode cooled in CO atmosphere; (B-F, black lines) CO stripping on a flame-annealed electrode cooled in Ar/H_2 atmosphere (CO adlayer deposited at 0.1 V_{RHE}). Insets: details of the CO pre-oxidation region. Data recorded in 0.1 M $HClO_4$ solution, at 50 mV s^{-1}.

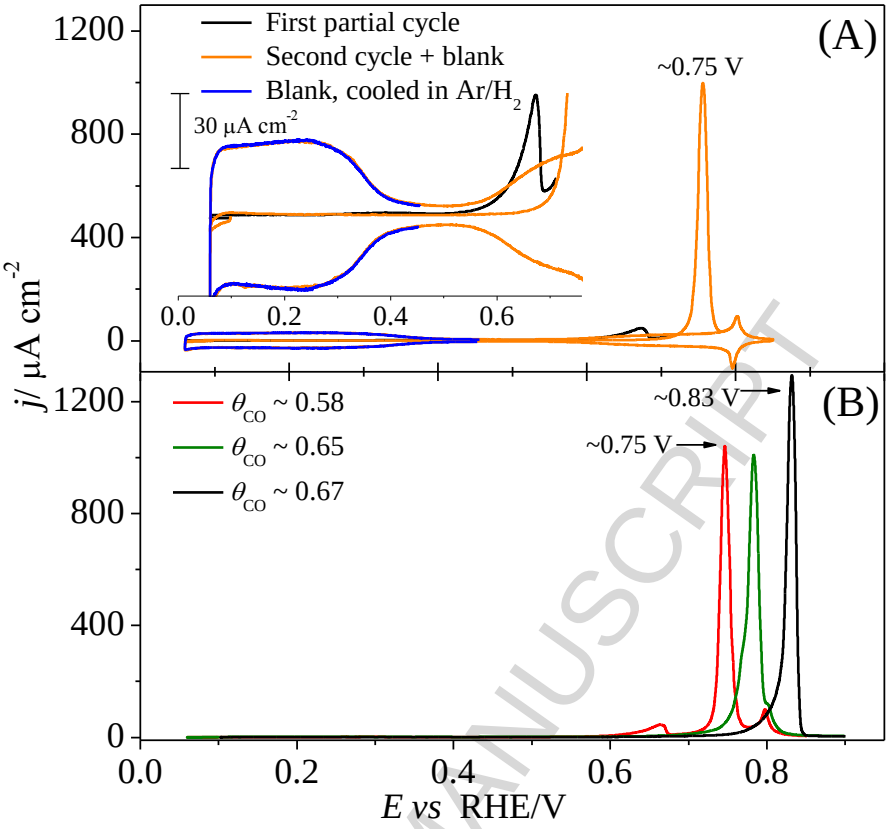


Figure 2. Pt(111) electrode, CO stripping. (A) – successive voltammetric cycles for the oxidation of a CO adlayer formed during cooling of the electrode in CO atmosphere: (black line) first partial cycle; (orange line) second cycle + subsequent cycle for recording of the blank voltammetry; (blue line) blank voltammogram for an electrode cooled in Ar/H_2. Inset: details of the voltammograms at low potentials. (B) – successive CO stripping: (red line) CO adlayer formed during cooling of the electrode in CO, successively without further flame annealed, (olive live) a new CO adlayer was deposited at 0.1 V_{RHE}; (black line) fresh electrode cooled in Ar/H_2. All data recorded in 0.1 M $HClO_4$, at 50 mV s^{-1}.

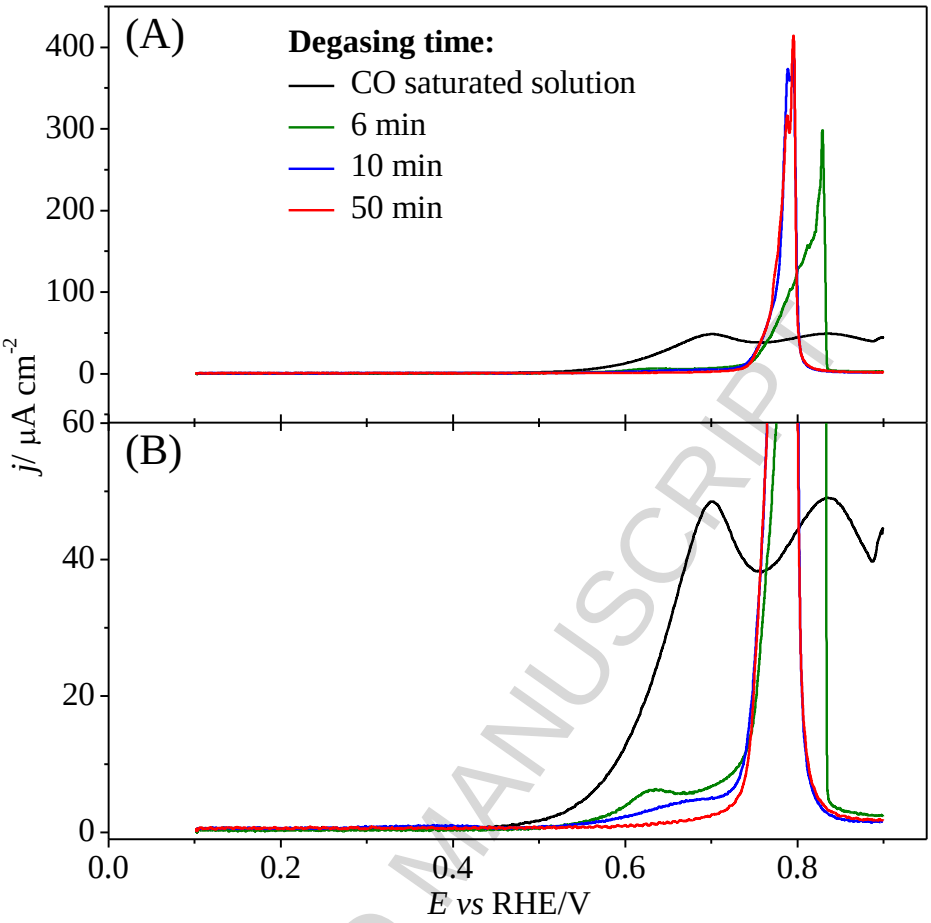
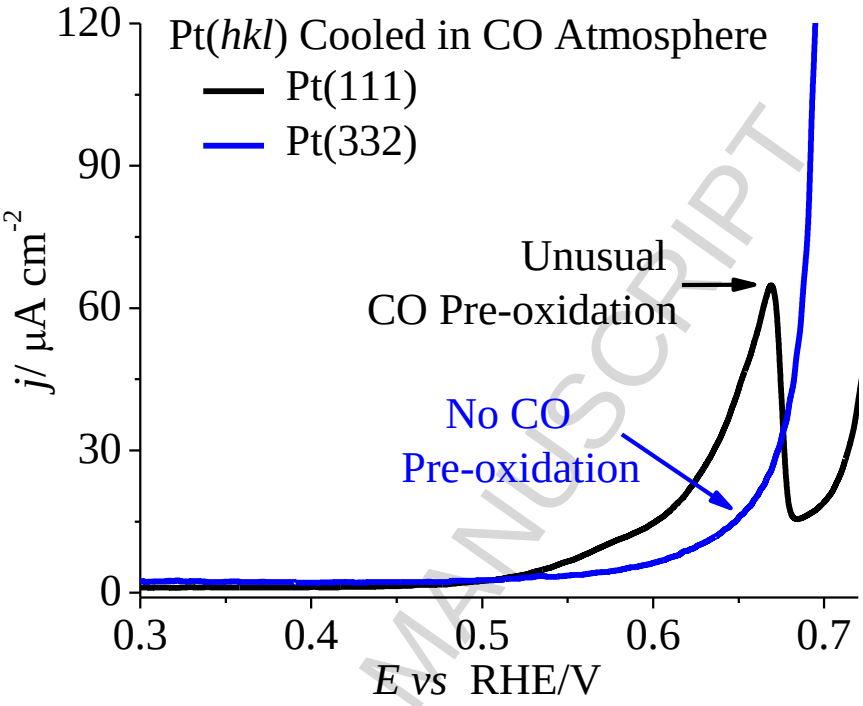


Figure 3. (A) Influence of dissolved CO on the voltammetric profile of CO electro-oxidation at a quasi-perfect Pt(111) electrode. The CO in solution was eliminated by bubbling Ar for different times (indicated). (B) Data in (A) presented using a different scale. Data recorded in 0.1 M $HClO_4$, at 20 mV s^{-1}.

Graphic Abstract



Highlights

- Unusual CO pre-oxidation on Pt(111) surfaces requires an *initial* long-range substrate.
- Unusual CO pre-oxidation is inhibited as the (111) planes become defect-rich.
- The activation pathway of CO pre-oxidation depended on the way that a CO adlayer was deposited on a Pt(111) surface.